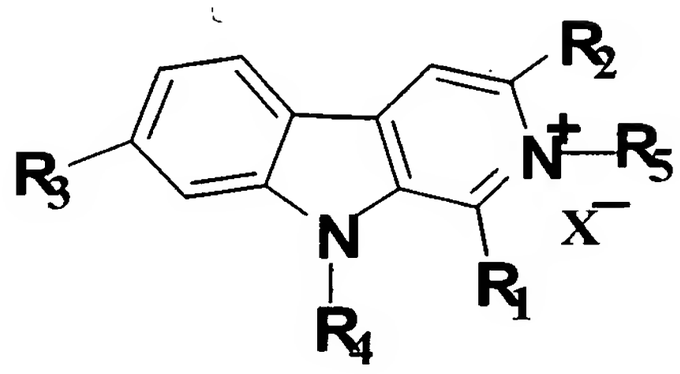
The Claims

1. A compound of the following formula (I)



wherein

R_1 is hydrogen, (secondary or tertiary) C_{1-6} linear or secondary or teriary branched alkyl, C_{6-10} arylalkyl or 1-5 halogenated arylalkyl, heterocyclic group or alkenyl;

R_2 is hydrogen, carboxyl, ester group, carboxylate, acylamino, acyl halide group or C_{1-6} alkoxycarbonyl, aryloxycarbonyl, or heterocyclic oxycarbonyl;

R_3 is hydrogen, hydroxyl, C_{1-6} alkoxy, carboxylic esters, carboxylic salts, arylalkoxy, or heterocyclic oxy group;

R_4 is hydrogen, C_{1-6} alkyl, C_{1-6} hydroxyalkyl, C_{6-10} arylalkyl or 1-5 halogenated arylalkyl, arylhydrocarbyl, arylcarboxyl, aryl ester group, arylamino group, arylnitro group, or heterocyclic group;

R_5 is hydrogen, C_{1-6} primary, secondary and tertiary linear or branched alkyl, C_{6-10} arylalkyl and 1-5 substituted arylalkyl, or heterocyclic group or alkenyl; and

R_1, R_2, R_3 and R_4 do not represent hydrogen at the same time, and

R_1, R_2, R_3 and R_4 do not represent hydrogen at the same time,

When R_2 and R_4 are hydrogen, R_1 is not methyl and R_3 is not methoxy;

When R_1 is methyl, R_2, R_3 and R_4 do not represent hydrogen at the

same time;

When R_1 is methyl, R_2 is hydrogen, and R_3 is methoxy, R_4 is not methyl, ethyl or butyl; and

When R_1 and R_3 are hydrogen, R_2 is not methoxycarbonyl and R_4 is not methyl.

2. The compound according to claim 1, characterized in that R_1 is hydrogen or C_{1-4} alkyl or C_{6-8} arylalkyl.

3. The compound according to claim 2, characterized in that R_1 is hydrogen or C_{1-2} alkyl.

4. The compound according to claim 3, characterized in that R_1 is hydrogen.

5. The compound according to claim 1, characterized in that R_2 is hydrogen or C_{1-4} alkoxycarbonyl.

6. The compound according to claim 5, characterized in that R_2 is hydrogen or C_{1-2} alkoxycarbonyl.

7. The compound according to claim 6, characterized in that R_2 is ethoxycarbonyl.

8. The compound according to claim 1, characterized in that R_3 is hydrogen, hydroxyl or C_{1-4} alkyloxy.

9. The compound according to claim 8, characterized in that R_3 is hydrogen.

10. The compound according to claim 1, characterized in that R_4 is hydrogen, C_{1-4} alkyl, C_{1-4} hydroxyalkyl or C_{6-8} arylalkyl or substituted arylalkyl.

11. The compound according to claim 10, characterized in that R_4 is hydrogen, C_{1-2} alkyl, C_{1-2} hydroxyalkyl or C_{6-8} arylalkyl or substituted arylalkyl.

12. The compound according to claim 11, characterized in that R_4 is ethyl or benzyl.

13. The compound according to claim 12, characterized in that R_4 is benzyl.

14. The compound according to claim 1, characterized in that R_1 is hydrogen, C_{1-4} alkyl or C_{6-8} arylalkyl, R_2 is hydrogen, or C_{1-4} alkoxycarbonyl, R_3 is hydrogen, hydroxyl, or C_{1-4} alkoxy, R_4 is hydrogen or C_{1-2} alkyl, C_{1-2} hydroxyalkyl, C_{6-8} arylalkyl or substituted arylalkyl.

15. The compound according to claim 14, characterized in that R_1 is hydrogen, R_2 is C_{1-2} alkoxycarbonyl, R_3 is hydrogen, and R_4 is C_{1-2} alkyl or C_{6-8} arylalkyl or substituted arylalkyl.

16. The compound according to claim 15, characterized in that R_1 is hydrogen, R_2 is ethoxycarbonyl, R_3 is hydrogen, and R_4 is ethyl or benzyl.

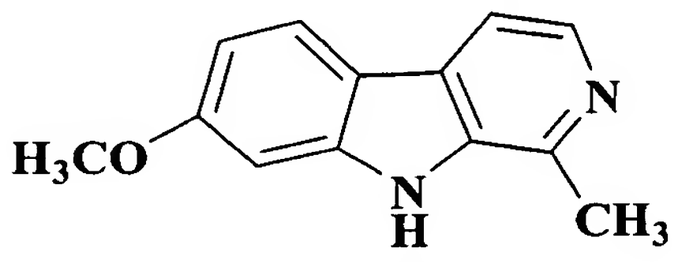
17. The compound according to claim 16, characterized in that R_1 is hydrogen, R_2 is ethoxycarbonyl, R_3 is hydrogen, and R_4 is benzyl.

18. The compound according to claim 1, characterized in that R_1 is methyl, R_2 is ethoxycarbonyl, R_3 is hydrogen, R_4 is pentafluorobenzyl, and R_5 is hydrogen.

19. The compound according to claim 1, characterized in that most preferably, R_1 is hydrogen, R_2 is hydrogen, R_3 is hydrogen, R_4 is benzyl, R_5 is benzyl, and X is bromine.

20. A process for preparing the compound according to claim 1 comprising the following steps:

1) dissolving harmines of the following formula 1 into an organic solvent or a mixed organic solvent;



1

2) adding 60% NaH and stirring it until there is no bubble formed;

3) adding halogenated alkane or halogenated aromatic alkane;

4) stirring and reacting said mixture at room temperature for 1-5 h; and

5) subjecting said mixture to conventional post-treatment and purification to produce 1,7,9-trisubstituted β-carboline derivatives.

21. A process for preparing the compound according to claim 1 comprising the following steps:

1) dissolving L-tryptophan and NaOH in water;

2) adding formaldehyde;

3) stirring and refluxing said mixture by heating for 3 h; and

4) subjecting said mixture to conventional post-treatment to produce 1,2,3,4-tetrahydro-β-carboline-3-carboxylic acid (9a).

22. A process for preparing the compound according to claim 1 comprising the following steps:

1) dissolving β-carboline-3-carboxylate into an organic solvent or a mixed organic solvent;

2) adding NaH and stirring it until there is no bubble formed;

3) adding halogenated alkane or halogenated aromatic alkane;

4) stirring and reacting said mixture at room temperature, or by heating for 2 to 5 h; and

5) subjecting said mixture to conventional post-treatment and purification to produce 9-substituted-β-carboline-3-carboxylates.

23. A process for preparing the compound according to claim 1 comprising the following steps:

1) dissolving 1-substituted-β-carboline-3-carboxylate into an organic solvent;

2) adding 60% NaH and stirring it for 5 minutes;

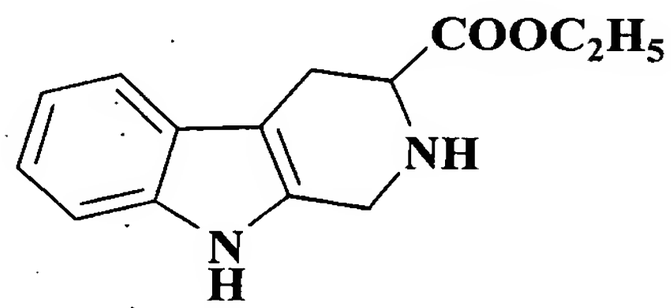
3) adding halogenated alkane or halogenated aromatic alkane;

4) reacting said mixture at room temperature, or refluxing said mixture by heating; and

5) after the reaction is finished, subjecting said mixture to conventional post-treatment and purification to produce 9-substituted-1-methyl-β-carboline-3-carboxylates.

24. A process for preparing the compound according to claim 1 comprising the following steps:

1) mixing compound 10b of the following formula with glacial acetic acid,



10b

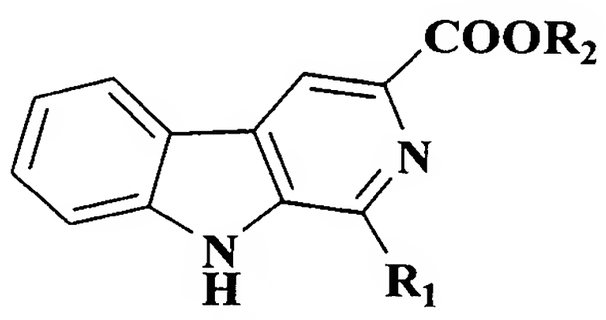
2) adding selenium dioxide;

3) refluxing said mixture by heating for 12 h; and

4) subjecting the mixture to conventional post-treatment and purification to produce β-carboline.

25. A process for preparing the compound according to claim 1 comprising the following steps:

1) mixing compound 10 of the following formula with an organic solvent and 60% NaH;



10

wherein R_1=H and R_2=C_2H_5;

2) stirring and reacting said mixture at room temperature for 5

minutes;

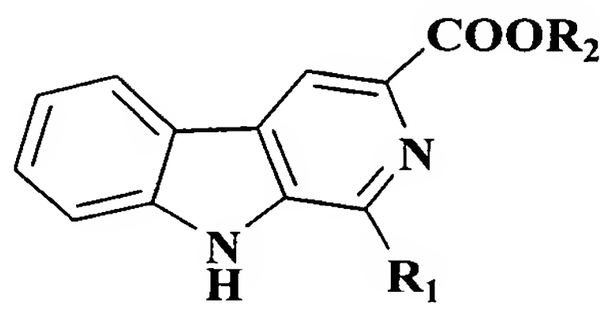
3) adding benzyl iodide;

4) stirring and reacting the mixture at a temperature of from 50 to 70℃ for 2 h; and

5) subjecting the mixture to conventional post-treatment and purification to produce 2,9-dibenzyl-3-ethoxycarbonyl-β-carbolinium iodate.

26. A process for preparing the compound according to claim 1 comprising the following steps:

1) mixing compound 10 of the following formula with an organic solvent and 60% NaH;



10

wherein R_1=H and R_2=C_2H_5;

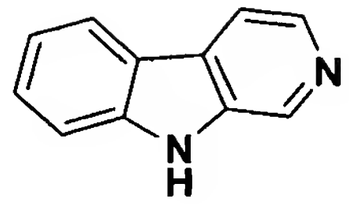
2) adding benzyl bromide;

3) stirring and reacting said mixture at a temperature of from 50 to 70℃ for 5 h; and

5) subjecting the mixture to conventional post-treatment and purification to produce2,9-dibenzyl-3-ethoxycarbonyl-β-carbolinium bromate.

27. A process for preparing the compound according to claim 1 comprising the following steps:

1) mixing compound 80 of the following formula with an organic solvent and 60% NaH;



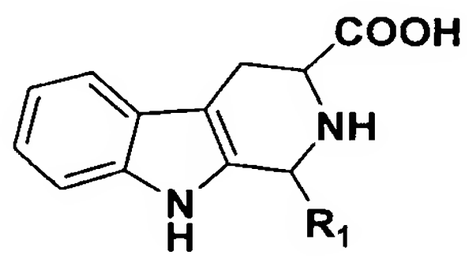
80

2) adding benzyl bromide or benzyl iodide;

3) stirring and reacting said mixture at a temperature of from 50 to 70℃ for 5 h; and

4) subjecting the mixture to conventional post-treatment and purification to produce 2,9-diphenylmethyl-β-carboline bromide or iodide salts.

28. A compound of the following formula (9a-16a):

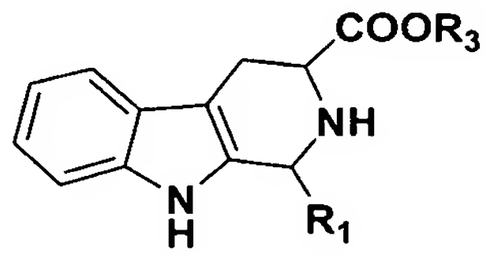


9a-16a

wherein

R_1 is methyl, ethyl, propyl, isopropyl, *n*-butyl, unsubstituted or halogenated phenyl, phenylmethyl, or phenylpropyl.

29. A compound of the following formula (9b-16b):

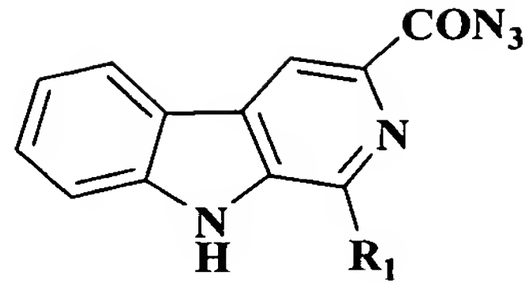


9b-16b

wherein

R_1 and R_3 are the same as R_1 defined in claim 26.

30. A compound of the following formula (21a):

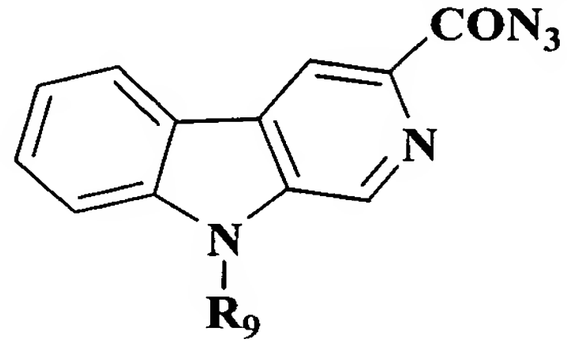


21a

wherein

R_1 is the same as R_1 defined in 26.

31. A compound of the following formula (53a-55a):

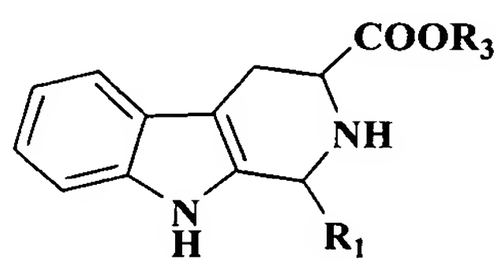


53a- 55a

wherein

R_9 is methyl, ethyl, n-butyl, phenylmethyl, phenylpropyl, polyhalogenated phenylmethyl or polyhalogenated phenylpropyl.

32. A compound of the following formula (10b):



10b

wherein

R_1 and R_3 are the same as R_1 defined in 26.

33. Use of a compound of any one of claims 1 to 18 in the manufacture of a medicament for treating tumors.

34. Use of a compound of any one of claims 1 to 18 in the manufacture of a medicament combined with phototherapy and radiation therapy for treating tumors.